Chapter 10
Upgrading of Oil Palm Biomass to Value-Added Products

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Abstract Indonesia and Malaysia account for about 85 % of the global palm oil production. Oil palm plantations in these two countries are producing about 200 million tons dry oil palm biomass and substantial amount of palm oil mill effluent (POME) which is rich in nutrients and carbohydrates. The solid oil palm biomass has been converted to a series of value-added products, such as solid fuels, biofertilizer, wood products, biocomposite, fiber mats and activated carbon, etc. POME, on the other hand, has been converted to biogas and biohydrogen for power generation. Recently, oil palm biomass has been explored as a possible feedstock for the production of biofuels, such as ethanol, butanol, syngas, and bio-oil. In addition, oil palm biomass has also been investigated for the production of value-added chemicals, e.g., volatile fatty acids, citric acid, levulinic acid, lactic acid, biodegradable

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plastics polyhydroxyalkanoates (PHAs), nanomaterials, and xylooligosaccharides. Although various value-added products have been investigated, the ultimate valorization of oil palm biomass will be possible if biorefinery approach is taken.

Keywords Oil palm biomass • Palm oil mill effluent • Value-added products • Biofuels • Bio-based chemicals • Biorefinery

10.1 Introduction

Global production of palm oil will reach 56 million metric tons in 2013, which has almost doubled over the past 10 years. By 2020, another 40 % growth is expected from its current levels and it will reach 78 million metric tons. In 2013, about 85 % of the global palm oil production is from Indonesia (29 million tons) and Malaysia (19 million tons) according to International Institute of Sustainable Development. With the rapid expansion of this industry, vast amount of oil palm biomass is generated. It was estimated that for one metricton of crude palm oil produced, approximately 4 tons of dry biomass are generated (Husin et al. 2002; Wahid et al. 2004; Yusoff 2006). Therefore, approximately 200 million tons of dry oil palm biomass is produced in Malaysia and Indonesia in 2013. Among the dry oil palm biomass, 75 % is left in the plantations as oil palm fronds (OPF) and oil palm trunks (OPT), and the remaining 25 % is generated in palm oil mills as empty fruit bunch (EFB), palm kernel shells (PKS), and mesocarp fiber (MF). In addition, significant amount of palm oil mill effluent (POME) is produced in palm oil mills (Tables 10.1 and 10.2).

Currently, majority of the oil palm biomass is returned to the field as biofertilizer to release its nutrients and replenish the soil, with a small increasing amount processed to wood products and bioenergy. In palm oil mills, EFB, PKS, and MF are burned for steam generation and power supply. POME is used for biogas production and power generation. Besides the above, oil palm biomass can also be potentially valorized to produce higher value products, such as pellets, biofuels, bio-based chemicals, and bio-based materials. This paper aims to review and discuss the potential routes to valorize oil palm biomass.

10.2 Direct Utilization of Oil Palm Biomass

Direct utilization of oil palm biomass refers to the utilization of such biomass in its polymer form without serious biomass decomposition. The major applications in such category are summarized in Fig. 10.1. This particularly refers to the solid oil palm biomass.

The most straight forward utilization of oil palm solid biomass is biofertilizer. For example, the major utilization of OPT and OPF is to shred them and return them to oil palm plantation as mulch. Young palms are planted directly onto the

Table 10.1 Types of oil palm biomass

Image	Biomass type	Description	Site of production
	Fronds (OPF)	Leaves of oil palm tree	Plantation
	Trunks (OPT)	Tree trunks available at end of plantation lifecycle	Plantation
	Brunches (EFB)	Remains after removal of palm fruits	Mill
	Shells (PKS)	Remains after palm kernel oil extraction	Mill
	Fiber (MF)	Remains after oil extraction from mesocarp	Mill
	Palm oil mill effluent (POME)	Liquid by-product from sterilization and milling process of fresh fruit bunch (FFB)	Mill

Table 10.2 Oil palm biomass availability in Malaysia in 2012

Biomass type	Availability[a] (million tons)
Fronds (OPF)	6.63
Trunks (OPT)	46.53
Brunches (EFB)	7.85
Shells (PKS)	4.77
Fiber (MF)	8.29
Palm oil mill effluent (POME)	66.27

Source: Malaysia Palm Oil Board (MPOB) 2012
[a]Dry weight

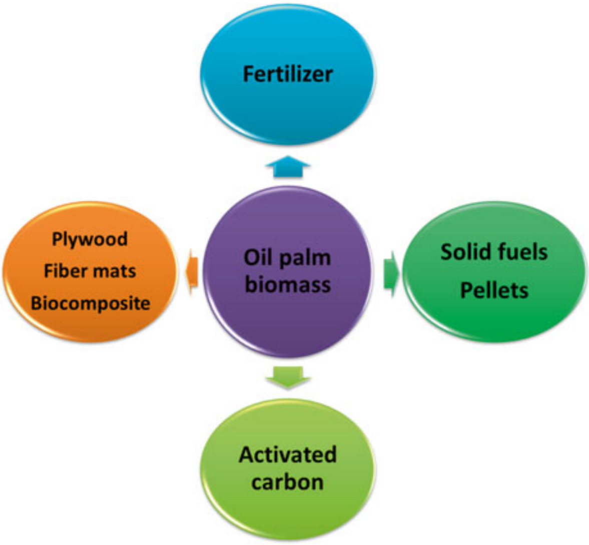

Fig. 10.1 Direct utilization of oil palm biomass

palm residue piles in order to increase the accessibility and efficiency of nutrient utilization. This way the palm oil yield was significantly improved compared with those planted in the area having no palm residue (Khalid et al. 2001). On the other hand, EFB is often composted to increase its digestibility and value as a biofertilizer (Oviasogie et al. 2010). EFB and its nutrients are mineralized into plant-available forms in the process of composting. In the meanwhile, pathogens are destroyed and disease infestation is suppressed by pressed partial sterilization. Mature compost is an excellent organic fertilizer and soil conditioner. When applied to and mixed into the soil, it can promote good soil composition, improve water and nutrient content, and assist erosion control. In the long term, it is beneficial to oil palm sustainable plantation.

Another common use of oil palm biomass is to use it as a renewable energy. For example, mesocarp fiber (MF) and palm kernel shells (PKS) generated by the palm oil mills are commonly used as solid fuels for steam boilers to generate electricity. This can generate enough energy to meet the energy demands of a palm oil mill, making it self-sufficient for energy supply in most palm oil mills. However, due to the incomplete combustion, dark smoke is produced while burning MF and PKS, causing environmental problems. On the other hand, most palm oil mills are using palm oil mill effluent (POME) for biogas production and POME-derived biogas is a good supplementary fuel for power generation in palm oil mills. It is likely to supply the excessive power generated from palm oil mills to the pubic grid.

In order to produce a more generic solid fuel, oil palm biomass such as OPT, EFB, MF, and PKS can be further processed to pellets, which are rich in energy and therefore are high-quality burning fuels for power plants. Palm pellets can substitute for coal and fuel oil as a burning biofuel, as well as bio-based raw material for industrial processes. Oil palm biomass pelleting is a relatively mature technology, which includes crushing, drying, pelleting, cooling, and packing. Due to the abundant resources of oil palm biomass in Malaysia and Indonesia, pellet manufacturers are gathered in this region and they are providing oil palm pellets to overseas markets, such as Europe and South Korea. Besides pelleting, oil palm biomass can be further processed through torrefaction to increase its energy capacity (Lu et al. 2012; Daud et al. 2013). In torrefaction raw biomass is heated in a nonoxidizing atmosphere in the temperature range of 200–300 °C. The main advantage of torrefaction is the amplification of the energy density of biomass.

Apart from fertilizer and renewable solid fuel application, a higher value utilization of oil palm biomass is to process it to wood products, such as plywood, fiber mats, biocomposite, and other bioproducts such as activated carbon. Plywood has been successfully produced from oil palm trunk in combination with the hardwood by the conventional plywood manufacturing process with modifications (Anis et al. 2003; Hashim et al. 2004). Empty fruit bunch is composed of 100 % organic fiber. It is hard and strong. It can be spun and woven into matting. Such palm fiber mats have the right strength and durability to protect the slopes from erosion, while allowing vegetation to flourish. They are commonly used as mulch and for erosion control. In addition, they are also used in highway/railway embankments, drainage channel banks, and in residential areas for beautification and landscaping. More recently, oil palm empty fruit bunch was investigated as a raw material for biodegradable polymer production. Hybrid biocomposite was prepared through the melt and blending techniques with poly(butylene adipate-co-terephthalate) (PBAT) (Siyamak et al. 2012), poly(3-hydroxybutyrate-co-38 mol%-3-hydroxyvalerate) [P(3HB-co-38 mol%-3HV)] (Salim et al. 2011), and polylactic acid (Mohamad Haafiza et al. 2009). The primary advantages of such oil palm fiber-based hybrid composites are its low densities, nonabrasiveness, and biodegradability. In addition, compared with the synthetic biodegradable plastics, such as polylactic acid (PLA), or polyhydroxyalkanoates (PHAs), the hybrid biocomposite made of natural biopolymers is more environmentally friendly and more cost-effective (Figs. 10.2 and 10.3)

In recent years, there has been an increasing interest in converting of oil palm biomass to activated carbon. Activated carbon can find wide applications as adsorbents, catalysts, or catalyst supports. Activated carbon is one of the most important adsorbents from an industrial point of view. It plays a vital role in removal various pollutants from gaseous and liquid phase mixtures. However, the usage of commercial activated carbon is restricting due to the use of non-renewable and expensive raw material such as coal. Therefore, in recent years, many researchers are trying to

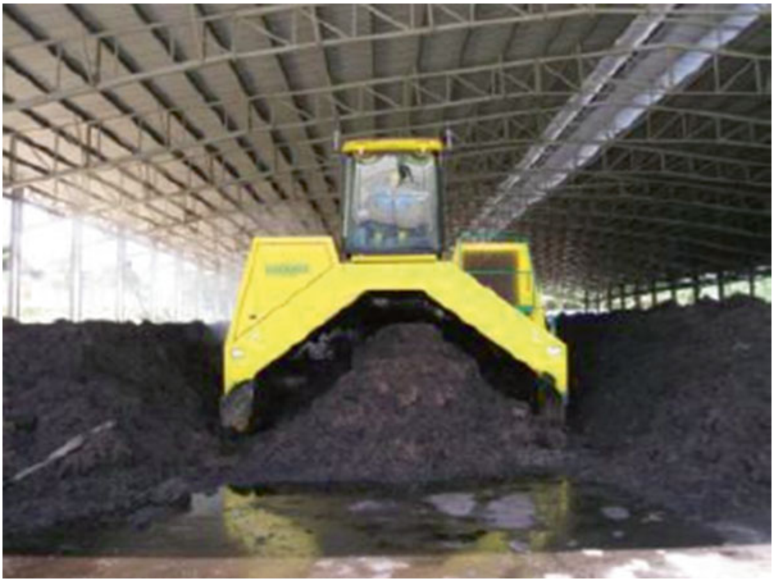

Fig. 10.2 EFB compost at Sime Darby palm oil mill

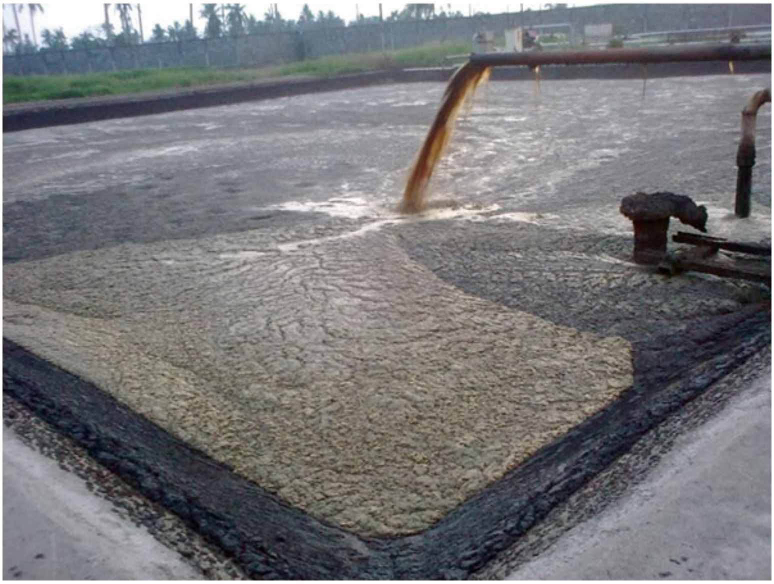

Fig. 10.3 Palm oil mill effluent

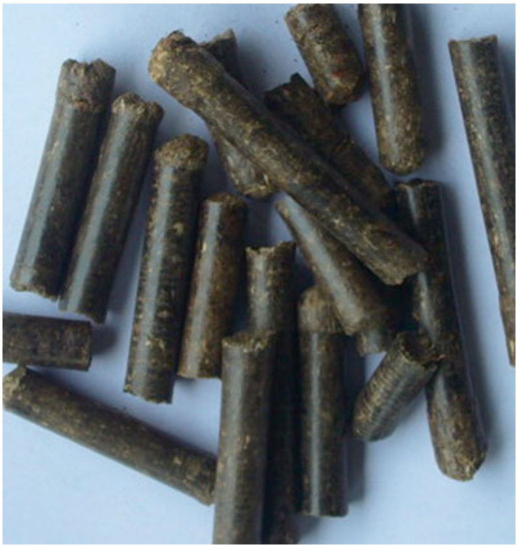

Fig. 10.4 EFB pellets

produce low-cost-activated carbons using renewable and cheaper precursors, such as industrial and agricultural by-products. For example, oil palm empty fruit bunch was converted to activated carbon through a thermal carbonization process and it was successfully used for 2,4,6-trichlorophenol removal from wastewater (Hameed et al. 2009) and for its application in super capacitors (Farma et al. 2013). A comprehensive review on activated carbon from oil palm biomass was given by Rafatullah and his colleagues (Rafatullah et al. 2013). By reviewing about 200 recently published articles, it was demonstrated that activated carbons from oil palm biomass exhibited outstanding capabilities for pollutants removal from gas and liquid mixtures and the performance are comparable to those from their commercial counterpart. Therefore, converting of oil palm biomass to activated carbon may provide a good opportunity to small and medium enterprises (SMEs) to valorize oil palm biomass. The challenge might be the cost involved in activated carbon preparation from oil palm biomass as thermal carbonization process is expensive and energy intensive. Further research is necessary to assess the economic feasibility and the environmental impact of the activated carbons produced by oil palm biomass (Rafatullah et al. 2013) (Fig. 10.4).

10.3 Conversion of Oil Palm Biomass to Biofuels

Oil palm biomass is lignocellulosic material containing three main structural components: cellulose, hemicellulose, and lignin. It also contains extractives. The chemical compositions of different parts of oil palm biomass are summarized in Table 10.3.

Table 10.3 Composition of oil palm biomass (Hashim et al. 2011)

		Chemical composition (%)		
Parts of oil palm biomass	Extractives	Cellulose	Hemicellulose	Lignin
Oil palm bark	10.00	18,87	58.95	21.85
Oil palm leaves	20.60	44.53	3.17	27.35
Oil palm frond	3.5	47.76	35.37	20.15
Oil palm shells	–	29.70	18.00	53.40
Mid part of oil palm trunk	14.50	50.21	22.39	20.15
Core-part of oil palm trunk	9.10	43.06	7.67	22.75
Oil palm empty fruit bunch	3.21	50.49	29.6	17.84

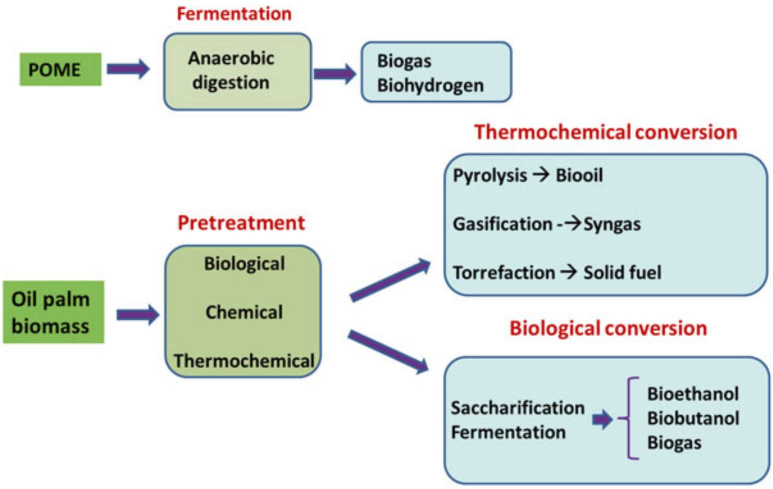

Fig. 10.5 Biofuel production from oil palm biomass

Over the past decade, oil palm biomass has been extensively explored as a feedstock for biofuel production. Generally speaking, oil palm biomass-based biofuel production-related activities can be summarized in Fig. 10.5.

10.3.1 Pretreatment of Solid Oil Palm Biomass

Similar to biofuel production from other lignocellulosic biomass, solid oil palm biomass conversion to biofuels can be classified into thermochemical conversion and biological conversion. Prior to each of the conversion technology, biomass pretreatment is necessary to reduce the recalcitrance of biomass and to enhance its converting efficiency. The purpose of pretreatment is to open its structure and increase its digestibility and subsequently the degree of conversion. Oil palm biomass pretreatment can be classified into biological pretreatment, physical pretreatment, chemical pretreatment, and physical–chemical pretreatment. For biological pretreatment, oxidizing enzymes and white-rot fungi were used to degrade the lignin content in EFB (Syafwina et al. 2002; Amin et al. 2010). Chemical method is the most often used pretreatment method for oil palm biomass, such as two-stage dilute acid hydrolysis (Millati et al. 2011), alkali pretreatment (Han et al. 2011), sequential dilute acid and alkali pretreatment (Kim et al. 2012), alkali and hydrogen peroxide pretreatment (Misson et al. 2009), sequential alkali and phosphoric acid pretreatment (Kim et al. 2012), aqueous ammonia (Jung et al. 2011a), and solvent digestion (Abdullah et al. 2011). However, it seems that alkali pretreatment is the most effective pretreatment method for oil palm biomass according to what is reported in the literature. Han and his colleagues investigated NaOH pretreatment of OPEFB for bioethanol production and a total glucose conversion rate (TGCR) of 86.37 % was obtained (Han et al. 2011). Lignin degradation might contribute to the effectiveness of alkali pretreatment and H_2O_2 posttreatment can further enhance such effects. Physical–chemical pretreatment such as ammonium fiber explosion (AFEX) (Lau et al. 2010) and superheated steam (Bahrin et al. 2012) was also effective in the increase of oil palm biomass digestibility.

10.3.2 Thermochemical Conversion of Solid Oil Palm Biomass

Thermochemical conversion of biomass refers to heating the biomass materials in the absence of oxygen to produce a mixture of gas, liquid, and solid. Such products can be used as fuels after further conversion or upgrading. It can be further classified as pyrolysis, gasification, and torrefaction. Pyrolysis refers to the thermal degradation of the biomass materials in the absence of oxygen conducted at 400–600 °C with short retention time. Its produces a mixture of liquids (water, oil/tars), solids (charcoal), and gases (methane, hydrogen, carbon monoxide, and carbon dioxide) and the composition of such mixture depends on the process parameters. Oil palm EFB fast pyrolysis was investigated using a bench top fluidized bed reactor with a nominal capacity of 150 g/L (Sulaiman and Abdullah 2011). It was found that higher temperature was more favorable for gas production. The bio-oil contained an organic phase predominated by tarry organic compounds (60 %) and an aqueous phase (40 %). The high viscosity of the organic phase and the high water content of the aqueous phase make bio-oil a challenging fuel for boilers and engines. It is worthwhile mentioning that Canada-based Dynamotive and Genting Bio-Oil Sdn Bhd (GBO) of Malaysia is collaboratively running a bio-oil pilot plant in Malaysia using oil palm EFB as the feedstock with the aim to commercialize this technology (Genting Group 2005).

Gasification process is an extended pyrolysis process conducted at elevated temperature range of 800–1,300 °C, which is more favorable to gas production. The gas stream is mainly composed of methane, hydrogen, carbon monoxide, and carbon dioxide. Biomass gasification offers a few advantages, such as less CO_2 emission, smaller footprint for equipment, easy combustion control, and high thermal efficiency. Gasifier design is very critical to ensure minimum energy consumption. Ogi et al. explored EFB gasification using an entrained-flow gasifier at 900 °C (Ogi et al. 2010). More than 95 % (C-equivalent) carbon conversion rate was obtained and the produced gas is rich in hydrogen making it suitable for liquid fuel synthesis. Oil palm EFB was proved to be an ideal candidate for biomass gasification. Oil palm EFB gasification was also investigated in a pilot-scale air-blown fluidized bed reactor (Lahijani and Zainal 2011). Compared to saw dust, at 1,050 °C, oil palm EFB had almost equivalent gas yield and cold gas efficiency. However, the produced gas had lower maximal heating values and higher carbon conversion. It was found that at high temperature, agglomeration was a major issue in EFB gasification. A bench scale fluidized-bed reactor was used for hydrogen-rich gas production (Mohammed et al. 2011a). The increase of temperature greatly enhanced the total gas yield. The gas yield reached the maximum value (~92 wt%) at 1,000 °C and mainly contained H_2 (38.02 vol.%) and CO (36.36 vol.%), making it suitable for further processing to other hydrocarbons. Oil palm EFB was an ideal biomass for gasification due to its high content of volatiles and in turn its high reactivity. At 700 °C, more than 90 % of oil palm EFB was decomposed (Mohammed et al. 2011b). A thermochemical analysis demonstrated that the heating value (HHV), specific heat (c), combustion rate (CR), combustion heat (Q) of the oil palm biomass displayed an increasing trend in the order of EFB, PKS, and MF (Nyakuma et al. 2013). Recently, both oil palm fronds (OPF) (Guangul et al. 2012) and oil palm trunk (OPT) (Nipattummakul et al. 2012) were investigated for gasification and syngas production and it was demonstrated both OPF and OPT were potential in syngas production. Therefore, we can conclude that all solid oil palm biomass are potential feedstock for biomass gasification and syngas production.

Torrefaction removes oxygen from biomass and therefore increases biomass energy density through the thermal process without oxygen. Through torrefaction, EFB, MF, and PKS were processed to potential solid fuels, with MF and PKS exhibited higher energy yield than EFB (Uemura et al. 2011a, b).

The above analysis suggests that thermochemical methods can convert almost all solid oil palm biomass to biofuels and gasification seems to be most suitable. Bio-oil application as a biofuel might be challenging due to its complex composition, high viscosity of the organic phase, and high water content of the aqueous phase.

10.3.3 Biological Conversion of Oil Palm Biomass

Biological conversion of oil palm biomass refers to the extraction of sugar from cellulose and hemicellulose, and then converting such sugar to biofuels through fermentation. It basically involves three major steps: pretreatment, saccharification, and fermentation. Biofuels obtained through oil palm biomass bioconversion include ethanol, butanol, biogas, and biohydrogen. Solid oil palm biomass is extensively studied as a potential feedstock for biofuel production, in particular, bioethanol production. On the other hand, palm oil mill effluent is often investigated for biogas and biohydrogen production.

EFB was pretreated by ammonium fiber expansion (AFEX) for cellulosic ethanol production (Lau et al. 2010). About 90 % of sugar yield was obtained after enzymatic saccharification. Up to 65 g/L glucose was obtained from the water extract of the AFEX-pretreated EFB (9 % solid loading) and it was fermented to ethanol within 24 h without the supplement of nutrients, suggesting its high ferment ability. An ethanol concentration of 18.6 g/L and a productivity of 0.11 g/L/h were obtained from aqueous ammonia soaking pretreated EFB (Jung et al. 2011a). This corresponds to an ethanol yield of 0.33 g ethanol/glucose. Han and his colleagues applied a pilot scale alkali pretreatment of EFB and through simultaneous saccharification and fermentation (SSF) processes, an ethanol titer of 48.54 g/L was obtained at 20 % (w/v) pretreated biomass loading (Han et al. 2011). By far, it is the highest ethanol titer from oil palm biomass. In total 410.48 g of ethanol were produced from 3 kg of raw EFB in a single run using this pilot scale facility. Aqueous ammonia method was also effective in oil palm trunk (OPT) pretreatment (Jung et al. 2011b), 95 % digestibility, and 13.3 g/L ethanol titer were obtained, corresponding to 78.3 % of the theoretical ethanol yield. Two-stage sulfuric acid pretreatment was also successfully applied to oil palm trunk to obtain bioethanol (Chin et al. 2010). Sime Darby Plantation and Mitsui Engineering and Shipbuilding of Japan announced a partnership that produced cellulosic ethanol from up to 1.25 metric tons of palm fruit waste per day in a pilot-scale project with an estimated 35–50,000 gal per year of ethanol (Biofuel Digest). This is the first and sole pilot-scale oil palm biomass to ethanol facility in the world and it was co-located with the Sime Darby's palm oil facilities at Selangor before (Biofuel Digest). Currently, this pilot scale cellulosic ethanol facility is with Tech Guan Group in Malaysia. The aim of the partnership between Mitsui and oil palm plantations in Malaysia is to gather data in support of a potential commercial scale-production facility. Cellulosic ethanol might be the first commercial biofuel from oil palm biomass, although it is not cost-effective compared to the first-generation bioethanol from sugarcane and corns. The advantage of the bioethanol is that it can be further processed to value-added chemicals such as ethylene, polyethylene, ethylene oxide, butanol, butene, butadiene, acetic acid, and ethyl acetate, etc., making cellulosic ethanol an attractive intermediate for value-added chemical production.

In terms of energy capacity and gasoline miscibility, butanol is better than ethanol as a biofuel. Although the advantages of butanol over ethanol are very well known, conversion of oil palm biomass to butanol is not fully explored, probably due to the low product concentration, low productivity, and low yield. EFB was pretreated by alkali followed by enzymatic hydrolysis. Approximately 20 g/L sugar was obtained and only about 1.262 g/L ABE (acetone: butanol: ethanol = 3:6:1) was attained using *Clostridium acetobutylicum* (Noomtim and Cheirsilp 2011). In another case, about 3.47 g/L ABE was obtained from EFB using *Clostridium butyricum* EB6 and it was found that cell growth was inhibited by the accumulated acid (5–13 g/L) (Ibrahim et al. 2012). Both of the above investigations obtained very low ABE concentration. Palm oil mill effluent (POME) has also been investigated as a substrate for butanol production and it was found that pretreatment is very essential for the increase of ABE concentration (Al-Shorgani et al. 2012). POME was pretreated with cellulolytic enzymes and XAD-4 resin, the production of ABE was increased to 4.29 g/L, corresponding to an ABE yield of 0.29 g/g. However, So far, there are no pilot scale facilities to convert oil palm biomass to butanol worldwide.

Palm oil mill effluent has high organic content and is therefore a potential substrate for biogas and biohydrogen production (Ji et al. 2013). Biogas generated from anaerobic digestion of POME can replace palm kernel shell (PKS) and mesocarp fiber (MF) as the boiler fuel for power generation. This way, excessive power generated at palm oil mills can be supplied to the pubic grid or nearby industries. Biogas production has been realized in a lot of palm oil mills (Ji et al. 2013). EFB has also been investigated for biogas production; however, pretreatment is necessary to improve its biogas yield (Nieves et al. 2011). Co-digestion of the pretreated EFB with palm oil mill effluent (POME) can further enhance the biogas production (O-Thong et al. 2012). Biohydrogen production is coupled with biogas production from POME in the anaerobic digestion process and its content was 57 % in the biogas produced (Vijayaraghavan and Desa Ahmad 2006). Pure culture of *Clostridium butyricum* EB6 was used and it seemed to be more favorable to biohydrogen production (Chong et al. 2009); biohydrogen production and productivity reached 3,195 mL H_2/L-medium and 1,034 mL H_2/L-medium/h, respectively. The produced biogas contained 60–70 % hydrogen. After cell immobilization in polyethylene glycol, the hydrogen production reached 5,350 mLH_2/L-POME, and the maximum H_2 production rate was 510 mL H_2/L-POME h (22.7 mol/L h) (Singh et al. 2013). Biohydrogen is produced in the commercial biogas production process as a co-product and pure culture biohydrogen production from POME has not been commercialized.

In summary, oil palm biomass has been extensively investigated for biofuel production, in particular EFB to bioethanol and POME to biogas. The highest ethanol titer, 48.54 g/L, was obtained by Han and his colleagues from alkali-pretreated EFB in a pilot scale reactor (Han et al. 2011) and a pilot scale cellulosic ethanol plant is currently run by Mitsui and Tech Guan Group, Sabah, Malaysia. The commercialization of oil palm biomass to ethanol technology largely depends on the process cost and ethanol yield; however, POME conversion to biogas has now become a reality in a lot of palm oil mills. Other than POME, prior to its bioconversion, the solid oil palm biomass such as OPT, OPF, PKS, MF, and EFB has to be pretreated to enhance their digestibility. While, alkali, aqueous ammonia, and dilute acid pretreatment methods were most often used in laboratory investigation, in industrial scale, steam explosion and hot water pretreatment are often reported, though they were not investigated in the lab scale for oil palm biomass bioconversion.

10.4 Conversion of Oil Palm Biomass to Bio-based Chemicals and Materials

Similar to biofuel production, conversion of oil palm biomass to bio-based chemicals can also be classified into two categories, i.e., thermochemical conversion and biological conversion. On the other hand, palm oil mill effluent (POME) can be

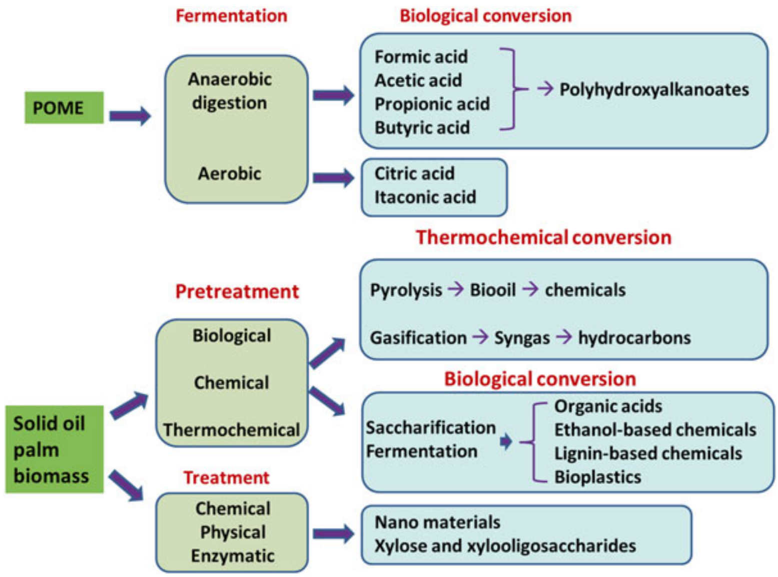

Fig. 10.6 Bio-based chemical and material production from oil palm biomass

converted to bio-based chemicals through anaerobic and aerobic fermentation. Substantial research has been done on the conversion of oil palm biomass to bio-based chemical and materials. It is summarized in Fig. 10.6.

10.4.1 Conversion of Palm Oil Mill Effluent to Bio-based Chemicals and Materials

Palm oil mill effluent (POME) is wastewater produced during the fresh fruit bunch sterilization and oil palm clarification (Borja et al. 1996). It has high chemical oxygen demand (COD), 100 times more than that for municipal wastewater. Raw POME contains 95–96%water, 0.6–0.7 % oil, and 4–5 % total solids (Wu et al. 2009). Reuse the effluent for biotechnological means not only can solve its environmental problems, but also create added value to palm oil mills. POME contains content of carbohydrate, protein, nitrogenous compounds, lipids, and minerals, making it an ideal fermentation media to produce some high value chemicals (Habib et al. 1997). Besides the intensive investigation of biogas and biohydrogen production, POME has also been explored as the feedstock to produce antibiotics, bioinsecticides, biopolymers (e.g., polyhydroxyalkanoates), organic acids, and enzymes so on and so forth (Wu et al. 2009). Among these, organic acids and polyhydroxyalkanoates are the two most extensively investigated fermentation products from POME.

10.4.1.1 Organic Acid Production from POME

A variety of organic acids, such as formic acid, acetic acid, propionic acid, and butyric acids, are produced in the anaerobic digestion of biological wastes (Mumtaz et al. 2008). The composition of such organic acids largely depends on the fermentation conditions. For example, acetic acid was predominant at higher pH, whereas formic acid was predominant at lower pH (Hassan et al. 1996). In addition, incorporating a sludge recycling system with the freezing–thawing method in the anaerobic treatment of POME was able to enhance organic acid production (Yee et al. 2003). Aerobic fermentation of POME has also been investigated to produce organic acids. POME with glucose and wheat flour as the co-substrates was used to produce citric acid using filamentous fungi *Aspergillus* strains with prolonged fermentation time (Jamal et al. 2005; Alam et al. 2008). More recently, it was found that cellulase digestion was an effective way to reduce the cost of citric acid production from POME (Nwuche et al. 2013). Itaconic acid was also produced from POME using an *Aspergillus* sp.; however, little itaconic acid could be obtained. Aerobic fermentation of POME for the production of either citric acid or itaconic acid not only depends on the fungal strains used, but also on the digestibility of POME. Enzymatic digestion is helpful in converting the polysaccharide components, such as cellulose and hemicellulose in POME, to fermentable sugars.

10.4.1.2 Polyhydroxyalkanoate (PHA) Production from POME

As mentioned above, a series of volatile fatty acids (VFAs), such as formic acid, acetic acid, propionic acid, and butyric acids, are produced in anaerobic digestion of POME. Such VFAs are potential platform chemicals for biofuel, chemical, and material production (Chang et al. 2010). Polyhydroxyalkanoates (PHAs) are 100 % biodegradable polymers that accumulate naturally in bacteria via fermentation from feedstock such as vegetable oils, sugar, or industrial wastes. It is likely to improve POME conversion efficiency and energy utilization further if bacterial PHA production can be integrated into the existing mill VFA-producing units (Mumtaz et al. 2010). Hassan and his research group have done so by combining the existing waste water treatment system with PHA production to achieve zero discharge for palm oil industry (Hassan et al. 2002). In POME anaerobic digestion, methanogenic activity was suppressed and organic acids were extracted. Such VFAs were then further separated, purified, clarified, and subsequently used for PHA production (Mumtaz et al. 2008; Sim et al. 2009). The effectiveness of PHA production from POME-derived VFAs depends on the VFA profiles, which in turn was determined by the pH value of the anaerobic process (Hassan et al. 1996). VFA concentration is also very critical and therefore VFAs need to be clarified and concentrated before their conversion to PHAs (Mumtaz et al. 2010). Several studies proved that polymers from POME-derived VFAs are comparable to those obtained from commercially available organic acids. In addition, PHA-producing microorganisms are also essential for the high-yield PHA production from such VFAs, where both pure culture and mixed culture have been investigated (Hassan et al. 2013). The advantage of using mixed microbial cultures is that anaerobic acidogenic fermentation (organic acid production) and aerobic PHA accumulation can be integrated to obtain simultaneous high COD removal and high PHA accumulation (Salmiati et al. 2007). However, it may increase the complexity of PHA recovery from cells. Therefore, further research and development on PHA production from POME should focus on the improvement of PHA content, volumetric productivity and quality while fulfilling the wastewater treatment objectives.

10.4.2 Conversion of Solid Oil Palm Biomass to Bio-based Chemicals and Materials

Apart from the palm oil mill effluent, palm oil mills and plantation generate tremendous amount of solid biomass such as oil palm frond (OPF), oil palm trunk (OPT), empty fruit bunch (EFB), palm kernel shell (PKS), and mesocarp fiber (MF), which contain significant amount of polysaccharides, such as cellulose and hemicellulose, and lignin (Table 10.3). Such solid oil palm biomass is the potential feedstock for bio-based chemical and material production. Similar to the case of biofuel production, both thermochemical and biological approaches can be used to convert solid oil palm biomass to bio-based chemical and materials (Fig. 10.6). Alternatively, like the case of POME, solid oil palm biomass can also be converted to a series of chemical materials through the VFA platform. Although over the past decade, such solid oil palm biomass has been extensively investigated for biofuel production, in particular, bioethanol production, only a few reports can be found on its conversion to bio-based chemicals and materials.

10.4.2.1 Thermochemical Conversion of Solid Oil Palm Biomass to Bio-based Chemicals

Oil palm biomass can be converted to bio-based chemicals through thermochemical processes. Oil palm EFB was pretreated using NaOH, H_2O_2, and $Ca(OH)_2$ to enhance its catalytic pyrolysis. Up to 90 wt% phenolic yields was obtained using Al-MCM-41 as the catalysts, whereas only 67 wt% phenolic yields were obtained for the untreated EFB (Misson et al. 2009). Phenols took up to 81 % of the liquid oil fraction of the pyrolysis product for the treated EFB. Besides phenol, the liquid oil also contained alcohols, acids, aldehydes, ketones, alkanes, alkenes and esters, etc. Such bio-oil fraction can be further upgraded to biofuels or bio-based chemicals. Lignin is a potential substitute for the expensive petroleum-derived phenolic compounds as it is an amorphous polymer composed of phenyl propane. EFB was converted to lignin through liquefaction process using ionic liquid and the highest lignin yield of 26.6 % was achieved at the optimum condition (Sidik et al. 2013). Lignin can be further converted to aromatic-based biochemical and biofuels through depolymerization in aqueous alkaline solution (Beauchet et al. 2012). Depending on the reaction conditions four fractions of products were obtained: (1) gas (mainly CO_2); (2) small organic compounds (methanol, acetic acid, formic acid, etc.); (3) aromatic monomers (up to 19.1 wt% of lignin); (4) oligomers (polyaromaticmolecules) and modified lignin (45–70 wt%). At high severities (315 °C) pyrocatechol was most abundant (up to 25.8 % selectivity). Using a hybrid catalyst comprising of modified zeolite and metal halide, EFB has also been converted to levulinic acid and up to 55.2 % oflevulinic acid yield was attained (Yaaini et al. 2012).

10.4.2.2 Biological Conversion of Solid Oil Palm Biomass to Bio-based Chemicals

Besides thermochemical conversion, biological conversion of the solid oil palm biomass to bio-based chemicals has also been investigated. As mentioned earlier, ethanol can be produced from oil palm biomass and such ethanol can be further processed to value-added chemicals such as ethylene, polyethylene, ethylene oxide, butanol, butane, butadiene, acetic acid, ethyl acetate, etc. In addition, oil palm biomass can also be converted to other chemicals through fermentation. Citric acid production from EFB was investigated through solid state fermentation using *Aspergillus niger* strains and up to 369 g citric acid was obtained from 1 kg dry EFB (Bari et al. 2009, 2010; Alama et al. 2010). Citric acid yield obtained using EFB was quite comparable to that obtained using other agricultural residues, such as rice straw. This suggests that citric acid production is an economic way to add value to such oil palm biomass. Lovastatin is a potent drug to lower the blood cholesterol levels and it was the first accepted statin as a hyper cholesterolemic drug by United States Food and Drug Administration (USFDA) (Tobert 2003). More recently, through solid state fermentation using *Aspergillus terreus*ATCC 20542, EFB was used to produce lovastatin and the yield of 70.17 mg lovastin/kg dry EFB was obtained when EFB was cofermented with soybean meal (Jahromi et al. 2012). Although the yield of lovastatin is low, it proves that it is possible to valorize such oil palm biomass to high value chemicals, such as pharmaceuticals. Bio-based chemicals can also be obtained by chemical or enzymatic hydrolysis of the oil palm biomass followed by bioconversion of the hydrolyzate. EFB was hydrolyzed using dilute H_2SO_4 and H_3PO_4 followed by over-liming using $Ca(OH)_2$. Such EFB hydrolyzate (containing mainly xylose) was used for lactic acid production using *Bacillus coagulans* JI12 and 59.2 g/L of lactic acid was produced within 9.5 h, with a lactic acid yield of 97 % and a productivity of 6.2 g/L/h (Ye et al. 2013). In a recent report, the enzymatic EFB hydrolyzate (containing mainly glucose and xylose) was used for polyhydroxybutyrate (PHB) using *Bacillus megaterium* R11 (Zhang et al. 2013). PHB content reached about 60 % in cell dry weight and 12.48 g/L PHB was obtained from EFB hydrolyzate containing 60 g/L sugar with PHB productivity of 0.260 g/L/h. Unlike EFB, oil palm frond (OPF) contains free sugars and OPF juice can be obtained by pressing the OPF using a sugarcane pressing machine (Zahari et al. 2012; Mohd Zahari et al. 2012). Such OPF juice contained a mixture of sugars such as glucose, sucrose, and fructose, where the glucose accounts for 70 %. OPF juice was used for PHB production, 2.72 g/L and 5.0 g/L of PHB was respectively obtained using *Cupriavidus necator* CCUG 52238 T (Zahari et al. 2012) and *Cupriavidus necator* CCUG52238 (Mohd Zahari et al. 2012). Further improvement of PHB production from OPF juice might be done through the use of high-content PHB-accumulating microbial strains and the optimization of fermentation conditions.

10.4.2.3 Value-added Material Production

In addition to bio-based chemicals, oil palm biomass has also been investigated for value-added material production. Sulfur-free chemical treatments were applied to oil palm EFB to generate cellulose pulps (Ferrer et al. 2012). Nanofibrillated cellulose (NFC) and nanopaper were produced from such cellulose pulps through microfluidization and over-pressing. The NFC grades compared fairly well with those produced from bleached wood fibers. Oil palm trunk (OPT) and oil palm frond (OPF) were used to produce fibrous materials (FM) and alkali-treated fibrous residues (FR) (Fung et al. 2010). The soluble fraction from alkali treatment of fibers was electrospun into nanofibers. Such nanofibers were further developed into nano encapsulants for drug delivery. As mentioned earlier, currently mesocarp fiber and palm kernel shell are mainly used as solid fuels for boilers in palm oil mills. After combustion, approximately 5 % ash is produced and such oil palm ash (OPA) can be further utilized for high-value material production. After high-energy ball milling, OPA was converted into a nano-structured materials and nano particles. The nano-structured OPA was suitable to be used as reinforcement for nanocomposites fabrication.

10.4.2.4 Xylose and Xylooligosaccharides Production

Sugar and sugar oligomers can be obtained from hydrolysis of solid oil palm biomass. As mentioned earlier, the key components of lignocellulosic biomass are cellulose, hemicellulose, and lignin (Table 10.3). Xylose is the main monomeric sugar in hemicellulose. Through chemical and biochemical processes, xylose can be used as a substrate for the production of a wide variety of compounds (Almeida e Silva et al. 1995), such as xylitol (Zhang et al. 2012). Xylitol can be used as an alternative sweetener and an anticariogenic agent. Dilute H_2SO_4 was used to treat oil palm empty fruit to extract xylose (Rahman et al. 2007). Xylose yield of 91.27 % and selectivity of 17.97 g/g were obtained under the optimal conditions. H_2SO_4 seemed to be better than H_3PO_4 in the recovery of xylose from oil palm EFB (Tan et al. 2013). Higher titer of xylose can be obtained if the solid loading can be further increased. Besides xylose, xylose oligomers or xylooligosaccharides (XOs) can also be obtained from hemicellulose. XOs are indigestible xylose-based oligomers. XOs have also been used in food ingredients, pharmaceuticals, feed formulations, and agricultural products (Vazquez et al. 2000; Moure et al. 2006). Oil palm fronds

[OPF] were investigated to produce XOs through auto hydrolysis followed by enzymatic treatment (Sabiha-Hanim et al. 2011). Autoclaving of palm fronds at 121 °C for 60 min recovered 75 % of the solid residue, containing 57.9 % cellulose and 18 % Klason lignin. The autohydrolyzate contained 14.94 % hemicellulose, corresponding to a fractionation efficiency of 49.20 %. The autohydrolyzate was hydrolyzed using 8 U of endoxylanase at 40 °C for 24 h and a solution containing 17.5 % xylooligosaccharides and 25.6 % xylose was generated. These results clearly indicate that OPF is a potential resource for XOs production. Oil palm EFB has also been investigated for xylooligosaccharides, in particular, xylobiose, production by chemical and enzymatic method (Lakshmi et al. 2012). Oil palm EFB was pretreated chemically and was then hydrolyzed using FXY-1 xylanase. A maximum 262 mg of xylobiose was produced from 1.0 g of pretreated EFB fiber corresponding to a xylobiose yield of 78.67 g/100 g (based on xylan in the pretreated EFB fiber). Further improvement in the yield of XOs might be obtained through thermochemical methods (Otieno and Ahring 2012).

10.5 Conclusion and Future Perspective

Oil palm biomass, including solid oil palm biomass and palm oil mill effluent, is a potential feedstock for value-added fuel, chemical, and material production. While the use of solid oil palm biomass as a fertilizer and mulch for oil palm plantation is well established, processing it to pellets, wood products, fiber mats, biocomposite, and activated carbon can bring more value to such biomass. Oil palm biomass pelleting, wood products, and fiber mats processing are relatively straight-forward, mature, and has been commercialized, whereas technology on biocomposite and activated carbon from oil palm biomass needs to be further improved to make it cost-effective. Despite the fact that biogas production from POME has been realized, biofuel production from oil palm biomass has not been commercialized though cellulosic ethanol and bio-oil technology are being demonstrated at the pilot scales. Commercialization of biofuel technology highly depends on the technology improvement and subsequent cost reduction. Citric acid production is probably the most mature bio-based chemical technology from oil palm biomass and it is quite commercializable as much similar citric acid yield was obtained using oil palm empty fruit bunch when compared to the use of other agricultural residue, such as rice straw. Although intensive research has been done on the conversion of POME to polyhydroxyalkanoate (PHA), due to the complexity of the process, low PHA content, and consequently low PHA yield, such process might not be commercialized in the near future. Similar to cellulosic ethanol technology, biological conversion of oil palm biomass to bio-based chemicals through saccharification followed by fermentation faces the problems of high cost due to the recalcitrance of the solid oil palm biomass. Biomass pretreatment and enzymatic saccharification should be improved to reduce the process cost. Alternatively, higher value chemicals, such as pharmaceutical products, can be produced from such processes to make them more economically feasible. Higher value products, such as nanomaterials, were produced using oil palm biomass; however, it is still at the initial stage. Although only a few studies reported the production of xylose and its oligomers from oil palm biomass, it is possibly a good technology to be commercialized as xylooligosaccharides can be used as ingredients in food and health-promoting products; therefore having higher value. Malaysia government is willing to mobilize 20 million tons of dryoil palm biomass for high value use (AIM 2011). However, it is unclear what high-value products can be firstly produced commercially from such biomass. Biorefinery of oil palm biomass to multiple value-added products, such as xylooligosaccharides, ethanol and ethanol-based chemicals, lignin and lignin-based chemicals, as well as animal feed or fertilizer from the fermentation residue, might be an ultimate solution.

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